



## Clothianidin Sorption in Missouri Wetland Soils

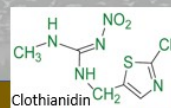
### Partition Coefficients

$(K_d)$  Solid-to-solution =

Concentration in  
soil

÷

Concentration in  
water



$(K_{oc})$  Organic carbon-to-solution =

$(K_d) * 100$

÷

Percent  
Organic  
Carbon

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## BACKGROUND INFORMATION

Neonicotinoid insecticides were introduced in the late 1990s and rapidly experienced wide-spread usage, due in part to their prophylactic use as an agricultural seed treatment. Physicochemical properties (e.g., high water solubility, long half-lives) of neonicotinoids enhance their environmental mobility which has led to detections in global surface waters and wetlands. Deleterious effects of neonicotinoids on non-target insects and wildlife emphasizes the need to determine management practices and environmental conditions that inhibit neonicotinoid mobility through soil. Clothianidin (CTN), introduced in 2003, is one of the most commonly applied neonicotinoid active ingredients. Clothianidin or thiamethoxam (which degrades to clothianidin) are routinely applied to >80% of corn seed planted in North America. Clothianidin is moderately water soluble and, while it has high leaching potential in soil, it can also accumulate and persist in the environment. Understanding CTN sorption (the process by which compounds are removed from solution to a solid phase) to wetland soils provides an indication as to whether the chemical is likely to remain mobile and more bioavailable in the environment. Solid-to-solution partition coefficients ( $K_d$  values) measure the amount of chemical substance adsorbed onto soil per amount of water. Values for  $K_d$  vary greatly among soil types due to specific properties of the soil under consideration (e.g., organic carbon content, clay content). Since adsorption occurs predominantly by partitioning onto or attaching to soil organic matter, it is also useful to express the partition coefficient in terms of organic carbon-to-solution ( $K_{oc}$  value). The objectives of this study were to 1) quantify CTN sorption by calculating  $K_d$  and  $K_{oc}$  values for Missouri wetland soils; and 2) examine the influence physical and chemical properties of Missouri wetland soil on CTN sorption.

## METHOD

Soil samples were collected from eight randomly selected wetland pools that contained hydric soil and were > 2 acres on seven MDC managed wetland conservation areas (CA) between mid-August and mid-October 2016. Soil samples were collected at a depth of 0-10 cm in locations that contained typical wetland vegetation (e.g., smartweed, nut sedge, cattails, etc.). No soil samples were collected from cropped areas within a wetland. We characterized each of the soil samples based on soil texture, organic carbon (OC), cation exchange capacity (CEC), and pH (CaCl<sub>2</sub>) to determine sorption capacity. Additionally, soil subsamples were sent to the University of Nebraska-Lincoln Water Sciences Laboratory to determine background pesticide concentrations; any residual concentrations were extracted using protocols described in Satkowski et al. (2018). We determined  $K_d$  values for the soil samples via single-point sorption experiments. We then conducted sorption isotherm experiments using the two most contrasting soils over a range of CTN concentrations to evaluate if there is an upper limit (within the range of concentrations evaluated) to the amount of CTN the soils can sorb.

## RESULTS

Results from the single-point sorption experiments indicate that CTN sorption to wetland soil is relatively weak (average  $K_d$  = 3.59 L kg<sup>-1</sup>); thus, CTN has potential to be mobile within Missouri wetland soils (Table 1). Based on linear regression analysis, no significant relationship was detected among  $K_d$  and  $K_{oc}$  values,

meaning  $K_{oc}$  values are not a useful parameter for predicting CTN sorption in these wetland soils. Surprisingly, none of the soil characteristics measured were significantly correlated with  $K_d$  values.

**Table 1.** Mean clothianidin solid-to-solution ( $K_d$ ) and organic carbon-to-solution ( $K_{oc}$ ) partition coefficients for soils collected from seven Missouri Department of Conservation managed wetland conservation areas (CA). Although  $K_d$  values vary based on soil type, typically, greater  $K_d$  values indicate more of the chemical is adsorbed to the soil surface and less likely to move in soil.  $K_{oc}$  measures the tendency of a chemical to sorb to carbon content; the greater the value, the more likely the chemical attaches to soil. Although no significant relationship was detected among  $K_d$  and  $K_{oc}$  values for wetland soils studied in this project, generally, a  $K_{oc}$  value <500 indicates the chemical is more likely to move with water than sorb to sediment.

Site Name	$K_d$ values L kg <sup>-1</sup>	$K_{oc}$ values L kg <sub>oc</sub> <sup>-1</sup>
B.K. Leach CA	4.70	206.99
B.K. Leach CA	2.08	97.39
Eagle Bluffs CA	4.16	282.75
Four Rivers CA	2.12	100.45
Marias Temps Clair CA	3.33	93.05
Nodaway Valley CA	5.87	213.50
Otter Slough CA	1.76	103.32
Ted Shanks CA	4.63	147.42
Average:	3.59	155.61

Sorption isotherms for two contrasting soils (from Otter Slough (OS) and Nodaway Valley (NV) CAs) indicated that, after a 24-hour incubation, a greater amount of CTN sorbed to NV soil whereas a greater amount of CTN remained in the liquid phase for OS soil. Based on the linear shape of the sorption isotherms, these soils have a high capacity to sorb CTN over the range of concentrations studied (0-2500 µg L<sup>-1</sup>).

## MANAGEMENT IMPLICATIONS

Results suggest that CTN has a weak affinity for the wetland soils studied and the soils are not limited in their capacity to sorb CTN over the range of concentrations studied (0-2500 µg L<sup>-1</sup>). These results support findings from Kuechle (Science Note 2019 vol 14 no 6) which suggests water and sediment neonicotinoid concentrations in Missouri wetlands were not in equilibrium. Both studies suggest that CTN remains highly mobile in wetland soils and that soil may serve as a persistent source of CTN to the water column and other wetland resources. Organic carbon content, clay content, CEC, and pH were not significantly correlated to  $K_d$  values, suggesting additional research may be important to understand if/how soil properties influence CTN sorption to wetland soils. Additional research would also be required to determine if there is an upper range to concentration at which CTN sorption to Missouri wetland soils plateaus or reaches capacity.

Literature Cited  
Satkowski, L.E., K.W. Goyne, S.H. Anderson, R.N. Lerch, E.B. Webb, and D.D. Snow. 2018. Imidacloprid sorption and transport in cropland, grass buffer, and riparian buffer soils. *Vadose Zone J.* 17:170139.

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